

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 265/02, C08K 7/02	A1	(11) International Publication Number: WO 90/08789 (43) International Publication Date: 9 August 1990 (09.08.90)
(21) International Application Number: PCT/US90/00413 (22) International Filing Date: 19 January 1990 (19.01.90) (30) Priority data: 304,616 24 January 1989 (24.01.89) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbot Rd., Midland, MI 48640 (US). (72) Inventor: TAI, Eva, F. ; 311 Seminole Court, Midland, MI 48640 (US). (74) Agent: BIEBER, James, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: AGGREGATES OR CLUSTERS OF WATER-SWELLABLE POLYMERS HAVING INCREASED HYDRATION RATE OVER UNASSOCIATED WATER-SWELLABLE POLYMERS (57) Abstract Clusters of water-swellaable polymer fines, having high rates of absorbency without gel-blocking are prepared by suspending water-swellaable polymer particles in an inert hydrophobic liquid, such as hydrocarbon, and slowly adding to the particles an aqueous solution, which can be water or an aqueous solution or mixture of water-soluble monomer and silica or a similar compound to silica.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LJ	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LJ	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

AGGREGATES OR CLUSTERS OF WATER-SWELLABLE POLYMERS
HAVING INCREASED HYDRATION RATE OVER UNASSOCIATED WATER-
SWELLABLE POLYMERS

Water-swellable polymers are well known in the
art as useful in diapers and various other devices where
5 aqueous absorption is desired. Often during the
production of such polymers, a variety of particle sizes
are produced. Those particles of very fine particle
size, smaller than 170 mesh (88 micrometers), do not
10 absorb moisture as desirably as larger polymer
particles. These fines are often separated and
discarded from the desirable larger particles. The
problem with the finer particles is thought to be gel
blocking, whereby an aqueous solution does not have
15 access to the polymer because of dense packing of the
particles and surface gelling of the polymer mass.

Therefore, it would be desirable to create a
method whereby such fine particles could be recycled or
20 reformed into useful water-absorbing polymer particles
rather than being discarded.

The present invention is a method for preparing
aggregates or clusters of water-swellable polymers,
25 having improved hydration rates and absorbing behavior,

comprising (a) suspending the polymer particles in an inert hydrophobic liquid, and (b) adding to the particles, slowly, under polymerization conditions, an aqueous solution or mixture such that said aggregates of the polymer are formed.

5

Preferably, the aqueous solution or mixture for binding the particles into aggregates or clusters comprises (i) at least one ethylenically unsaturated carboxylic acid which is polymerizable with the water-swella-
10 ble polymers and (ii) an amorphous, oil dispersible, substantially water-insoluble, particulate material.

15

Optionally, additional steps may include (c) drying the aggregates and (d) crushing the aggregates.

20

The present invention also includes aggregates or clusters of water-swella-
20 ble polymers, said aggregates having improved rates of hydration and absorbing behavior, characterized by: water-swella-
25 ble polymer particles associated by bonding to other water-swella-
ble polymer particles in a random packing configuration spacially distributed to allow aqueous absorption. The term "aggregates" in this application means discrete clusters of water-swella-
ble polymer particles. Permeated with many channels wherein a contacting aqueous fluid has access to and is absorbed by said
30 polymer.

The aggregates or clusters of the invention are typically comprised of water-swella-
ble polymer particles having a broad range of unassociated particle sizes of 20 mesh

-3-

(841 micrometers) to 400 mesh (37 micrometers). The water-swella-
ble polymer particles are associated or clustered by bonding to other water-swella-
ble polymer particles in a random packing configuration spacially
distributed to allow aqueous absorption, said aggregates
5 or clusters having a size of 300 micrometers to 3000 micrometers.

The present invention is also drawn to an absorbent article comprising aggregates or clusters of
10 water-swella-ble polymers formed by (i) suspending the unassociated polymer particles in an inert hydrophobic liquid, (ii) adding to the particles, slowly, under polymerization conditions, a solution or mixture
15 comprising at least one ethylenically unsaturated carboxylic acid that is polymerizable with the unassociated water-swella-ble polymers and an amorphous oil dispersible substantially water-insoluble particulate material and (iii) drying said aggregates.

20 The Figures included herewith illustrate the invention by means of pairs of photomicrographs of the unassociated particles and the aggregates or clusters, of said particles. The actual invention is represented
25 by the aggregates shown in Figures 2, 4, 6, 8 and 10. Figures 1, 3, 5, 7 and 9 depict the unassociated particles, and are not photographs of the present invention. Figure 1 is a photograph of unassociated water-swella-ble polymer particles having a size of
30 325 mesh (44 micrometers) and smaller and Figure 2 is a photograph of the aggregates or clusters of the unassociated particles having the particle size of 325 mesh (44 micrometers) and smaller. Figure 3 is a photograph of unassociated particles having a variety of

sizes and Figure 4 is a photograph of the aggregates of those unassociated particles having varying sizes.

Figure 5 is a photograph of unassociated polymer particles having a size of 170 to 325 mesh (88 to 44

micrometers) and Figure 6 is a photograph of the aggregates of the polymer particles having an unassociated particle size of 170 to 325 mesh (88 to 44

micrometers). Figure 7 is a photograph of unassociated polymer particles having a size of 100 to 170 mesh (149 to 88 micrometers) and Figure 8 is a photograph of the

aggregates of the polymer particles having an unassociated particle size of 100 to 170 mesh (149 to 88 micrometers). Figure 9 is a photograph of unassociated

polymer particles having a size of 50 to 100 mesh (297 to 149 micrometers) and Figure 10 is a photograph of the

aggregates of the polymer particles having an unassociated particle size of 50 to 100 mesh (297 to 149 micrometers).

A. The Water-Swellable Polymer Particles

The water-swellable or lightly crosslinked hydrophilic polymer particles useful in the present invention can be any of the known hydrophilic polymers which are capable of absorbing large quantities of fluids. Examples of such polymers include those disclosed in U.S. Patents 4,833,222, 3,997,484; 3,926,891; 3,935,099; 4,090,013; and 4,190,562. Such hydrophilic polymers are prepared from water-soluble α,β -ethylenically unsaturated monomers such as mono and polycarboxylic acids and acrylamide and its derivatives.

The water-soluble monomers which are polymerized to form the water-swellable polymers of the present invention include those monomers listed in U.S.

Patent 4,833,222. Examples of such monomers include α,β -ethylenically unsaturated monomers such as mono and polycarboxylic acids.

B. The Aggregates or Clusters

5

The water-swellaable or lightly crosslinked hydrophilic polymer particles which benefit the greatest from being incorporated into the aggregates or clusters of the present invention are those unassociated particles which have a mesh size of less than 400 mesh (37 micrometers) and , preferably, from 170 to 400 (88 to 37 micrometers). Such unassociated particles have been identified as causing gel blocking when such polymer particles are contacted with aqueous fluids. Gel blocking, it is thought, occurs when the polymer particles are small and fine, causing tight packing of a mass of unassociated particles. The particles of the mass of polymer are thought to be compacted to such an extent that swelling and gelling on the surface of the mass of polymer occurs when it is contacted with an aqueous fluid, blocking remaining aqueous fluid from freely flowing between the particles and being absorbed. These same unassociated particles do not exhibit gel blocking behavior when incorporated into the aggregates or clusters of the present invention.

The aggregates of water-swellaable polymers are comprised of water-swellaable polymer particles associated by being bound to other water-swellaable polymer particles in a random packing configuration spacially distributed to allow aqueous absorption. The packing configuration of the polymer particles described herein as "random packing configuration spacially distributed to allow aqueous absorption" is illustrated

in the photographs, Figures 2, 4, 6, 8 and 10. The Figures illustrate the particles of the aggregates or clusters as being bonded together in a random spacial distribution to allow for greater efficiency of aqueous absorption.

5

G. The Aqueous Solution

The aqueous solution can be (a) water or (b) an ethylenically unsaturated monomer dispersed in water.

10 When the aqueous solution comprises an ethylenically unsaturated carboxylic acid monomer, the monomer is polymerizable with the water-swellaable polymer of the present invention and includes all of those monomers described above as water-soluble monomers particularly
15 acrylic acid, methacrylic acid, crotonic acid, and isocrotonic acid, alkali metal salts and ammonium salts thereof. Suitable polycarboxylic acids include maleic acid, fumaric acid, and itaconic acid. Suitable
20 acrylamide derivatives include methacrylamide. The preferred monomers include acrylic acid and methacrylic acid and their respective salt forms such as alkali metal or ammonium salts.

25 Optionally a crosslinking monomer can be added to the aqueous solution. Organic compounds having two or more ethylenic groups copolymerizable with the water-soluble monomers can be used as the crosslinking monomers. Exemplary crosslinking monomers include
30 diacrylate or dimethacrylate of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, trimethylol propane and pentaerythritol; triacrylates or trimethacrylates of trimethylol propane and pentaerythritol; tetracrylates

-7-

or tetramethacrylates of pentaerythritol, N,N'-methylene-bis-acrylamide, N,N'-methylene-bis-methacrylamide and triallyl isocyanurate, and the like. The preferred crosslinking monomers for the present invention is trimethylolpropanetriacrylate. The particulate material can also be present in the aqueous solution or can be present in the polymer particle suspension as discussed below.

Optionally, minor amounts of other water-soluble, unsaturated monomers may be present in the aqueous solution such as alkyl esters of the acid monomers. For example, methyl acrylate or methyl methacrylate may be present.

D. The Polymer Particle Suspension

The inert hydrophobic liquid used to suspend the water-swellaable polymer particles and the aqueous solution of monomer is usually an organic compound which is normally liquid at the conditions at which the polymerization process occurs. Operable liquids include hydrocarbons or substituted hydrocarbons. Preferred organic liquids are the halogenated hydrocarbons such as perchloroethylene, methylene chloride and the like, as well as liquid hydrocarbon having from 4 to 15 carbons per molecule including aromatic and aliphatic hydrocarbons and mixtures thereof, e.g., benzene, xylene, toluene, mineral oils, liquid paraffins such as kerosene, naphtha and the like. Of the foregoing organic liquids, the hydrocarbons are the more preferred, with aliphatic hydrocarbons being most preferred.

The particulate material comprising a hydrophobic character is an amorphous, highly oil-dispersible, approximately micrometer and sub-micrometer size, substantially water-insoluble particulate material. Typically, the size of the particulate material ranges from less than one to several micrometers in diameter. The particulate material is most preferably hydrophobic silicon dioxide, for example, the particulate material provided by the reaction of silica with polydimethyldichlorosilane. Other useful particulate materials include hydrophobic clays such as the cationic surfactant treated bentonite clays. An example of a hydrophobic clay is sold commercially as Bentone® 34 by N. L. Industries.

The Process

Preparing the aggregates or clusters of the present invention requires suspending the aqueous absorbing polymer particles in the inert hydrophobic liquid. Typically, the weight ratio of polymer to liquid is not critical, however, for practical purposes the preferred ratio is in the range of from 1:10 to 10:1.

The aqueous solution can be water or can include an ethylenically unsaturated monomer. The ethylenically unsaturated monomer solution is typically prepared by first dispersing the monomer in water. The monomer can be preneutralized and exist as a salt or as a mixture of the acid and the salt, however if the monomer is in acidic form, the pH of the solution should then be adjusted to between 4 and 7. The weight ratio of monomer is typically 1:10 to 5:10 monomer to polymer particles. Preferably the weight ratio of monomer is

typically 2:10 monomer to polymer particles and the ratio of monomer to water is typically 0:10, preferably 4:10. Optionally, the aqueous solution (with or without the monomer) may also contain a crosslinker, chelating agent and initiator. Therefore, the total monomer, if present, is present in the range of 15 to 45 weight percent based on total weight of the solution. The crosslinker is typically added in an amount of 0 to 5 weight percent based on the total weight of the monomer.

5
10 The amorphous highly oil dispersible substantially water-insoluble particulate material is suspended in an inert hydrophobic liquid. The aqueous solution or aqueous monomer solution is then added to the particulate material to form a suspension of aqueous droplets or aqueous monomer droplets. The aqueous suspension or aqueous monomer suspension is then added slowly to the suspended polymer particles while the polymer particle solution is agitated and exposed to polymerization conditions. The polymerization temperature can range from 10°C to 100°C, depending upon initiators chosen.

25 The size of the aggregates or clusters formed will depend on the size of the polymer particles with which the process begins. However, a major contributor to the size of the aggregates or clusters is the size of the droplets of aqueous solution or aqueous monomer solution which are suspended in the inert hydrophobic liquid and added to the suspended particles solution. The droplet size is controlled by the amount of amorphous highly oil dispersible substantially water-insoluble particulate material present in the monomer solution. For example an aggregate of approximately 1000 micrometers can be formed when the

30

droplets are approximately 50 micrometers in diameter. This is achieved if the particulate material is present in a ratio of approximately 0.3 to 2 percent based on the weight of total polymer present.

- 5 The aggregates or clusters can be filtered from the inert liquid, dried in an oven and crushed to a desirable size.

- 10 The hydration rate of the aggregate polymer particles is tested by evenly spreading 1.0 g of polymer particles over the bottom of a medium sized plastic boat (Fischer catalog 500 ct. #682-160-502). 30 Grams of a 0.9 percent sodium chloride solution is poured over the particles and a timer is simultaneously set. The
15 hydration rate is that time required for the polymer to take up the solution and become stiff.

Examples

- 20 The following examples illustrate the present invention.

Example 1

- In a one liter reactor 80 grams of Drytech® polymer (sodium polyacrylate polymer manufactured by the
25 Dow Chemical Company), having a mixed particle size distribution, is mixed with 300 grams of Isopar M hydrocarbon (deodorized kerosene from Exxon). The dispersion is suspended using agitation. The monomer
30 phase is prepared with a solution of 12 grams of acrylic acid; 0.05 gram of trimethylolpropane triacrylate; 0.05 gram of a chelating agent; 15.7 grams of water; 12 grams of a 50 percent solution of sodium hydroxide; and 0.1 gram of t-butyl hydrogen peroxide, suspended as droplets in a solution of 100 grams of Isopar M hydrocarbon and 0.25 gram of hydrophobic fumed silica

5 sold as Aerosil R-972 from Degussa. The aggregates or clusters are formed by adding the monomer phase to the reactor under constant agitation at 600 rpm, 20°C and under the flow of sulphur dioxide gas between 0.1 to 10.0 ppm/min. The aggregates are then separated from the hydrocarbon by filtration and then dried in a hot air oven at 100°C overnight.

10 The hydration rate of the clusters or aggregates of the invention is tested by evenly spreading 1.0 g of clusters over the bottom of a medium sized plastic boat (Fischer catalog 500ct. #682-160-502). Thirty grams of a 0.9 percent sodium chloride solution is poured over the particles and a timer is
15 simultaneously set. The hydration rate is that time required for the aggregates to become stiff. The aggregates exhibited a hydration rate of 15 to 20 seconds with no visible gel blocking. A Comparative Example 1 of the Drytech® (The Dow Chemical Company)
20 non-clustered polymer fines having mixed particle size distribution exhibited a hydration rate of greater than 10 minutes with visible gel blocking.

25 The absorbent properties are determined by the following procedures:

1. Filtered Free Swell Capacity (FFSC) is determined by allowing 1.0 g of the polymer aggregates or clusters to absorb its limit of 200 g of 0.9 percent
30 sodium chloride solution in 30 minutes then filtered using a Buchner funnel and filter flask evacuated by an aspirator. The excess salt solution which is not absorbed and filtered is weighed and subtracted from the

original 200 g to yield the filtered free swell capacity value.

2. Water Soluble Polymer Content is determined by extracting 1 g of absorbent polymer for 16 hours with 500 g of 0.9 percent sodium chloride. The swollen polymer is filtered off and the filtrate titrated with hydrochloric acid to determine the level of soluble polymer present.

The cluster or aggregates polymer composition of this example of the invention exhibits a FFSC of 26 g/g and a water soluble polymer content of 7 percent.

Example 2

Polymer particles having a particle size of smaller than 325 mesh (44 micrometers) are associated similarly by the method used to produce the clusters of Example 1. The hydration rate, FFSC and water soluble levels of the aggregates are evaluated in a similar manner to those aggregates of Example 1. The hydration rate for the clusters of Example 2 is 15 to 20 seconds with no visible gel blocking, the FFSC is 28 and the water-solubles level is 7. Comparative Example 2, which consist of samples of the unassociated polymer particles having a particle size smaller than 325 mesh (44 micrometers), are evaluated in a similar manner to those of the Comparative Example 1. The samples of Comparative Example 2 exhibit gel blocking.

Example 2 and Comparative Example 2 illustrate that for particles of smaller than 325 mesh (44 micrometers), the aggregates or clusters of the invention exhibit a hydration rate of between 2 and

-13-

5 seconds whereas the unassociated particles of that same mesh size undesirably g l block.

5

10

15

20

25

30

1. A method for preparing aggregates or clusters of water-swellable polymer particles, having improved hydration rate and absorbing behavior, comprising: (a) suspending the water-swellable polymer particles in an inert hydrophobic liquid; and (b) adding to the particles, slowly, under polymerization conditions, an aqueous solution, or mixture such that said aggregates or clusters of the polymer are formed.
2. The method of Claim 1 wherein the aqueous solution comprises an ethylenically unsaturated carboxylic acid monomer of acrylic acid, methacrylic acid, crotonic acid, or isocrotonic acid.
3. The method of Claim 2 wherein the aqueous solution additionally comprises a crosslinking monomer consisting of diacrylate or dimethacrylate of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, trimethylol propane, pentaerythritol, triacrylates or trimethacrylates of trimethylol propane, pentaerythritol, tetracrylates or tetramethacrylates of pentaerythritol, N,N'-methylene-bis-acrylamide, N,N'-methylene-bis-methacrylamide, or triallyl isocyanurate.

-15-

4. The method of Claim 1 wherein the inert hydrophobic liquid is halogenated hydrocarbons or liquid hydrocarbons of 4 to 15 carbons per molecule.

5 5. The method of Claim 4 wherein said halogenated hydrocarbon is perchloroethylene or methylene chloride.

10 6. The method of Claim 4 wherein said liquid hydrocarbon is aromatic, aliphatic hydrocarbons or mixtures thereof.

7. The method of Claim 2 wherein the aqueous solution additionally comprises a particulate material of hydrophobic character.

15 8. The method of Claim 7 wherein the particulate material is hydrophobic silicon dioxide.

20 9. The method of Claim 2 wherein the ethylenically unsaturated carboxylic acid monomer is present in an amount of 15 to 45 weight percent, based on total weight of the aqueous solution.

25 10. The method of Claim 1 wherein the aqueous solution of step (b) is (i) at least one ethylenically unsaturated carboxylic acid that is polymerizable with the water-swella-
ble polymers and (ii) an amorphous, oil dispersible, substantially water-insoluble, particulate material.

30

12. Aggregates or clusters of water-swella-
ble polymers, said aggregates having improved rates of hydration and absorbing behavior, characterized by: water-swella-
ble polymer particles associated by bonding

to other water-swellaable polymer particles in a random packing configuration spacially distributed forming discrete clusters of water-swellaable polymer particles that allow aqueous absorption.

5 13. The aggregates or clusters of Claim 12 wherein the aggregates are comprised of water-swellaable polymer particles having an unassociated particle size of 20 mesh (841 micrometers) to 400 mesh (37 micrometers) and the water-swellaable polymer particle
10 clusters have a size of 300 micrometers to 3000 micrometers.

 14. A method of using the aggregates or clusters of Claim 12, comprising: combining said
15 aggregate with a fiber material; and forming said combination in an aqueous-absorbing article.

 15. An article including the aggregates or clusters of Claim 12.

20

 16. An absorbent article, comprising:

 (a) 50 to 98 percent by weight of said article of a hydrophilic fiber material; and

 (b) 50 to 2 percent by weight of said article
25 of aggregates of water swellaable polymers, formed by (i) suspending particles of said polymers in an inert hydrophobic liquid, (ii) adding to said suspension, slowly, under polymerization conditions, an aqueous solution or mixture of an ethylenically unsaturated
30 carboxylic acid that is polymerizable with the water-swellaable polymers and an amorphous, oil dispersible, substantially water-insoluble, particulate material, and (iii) drying said aggregate.

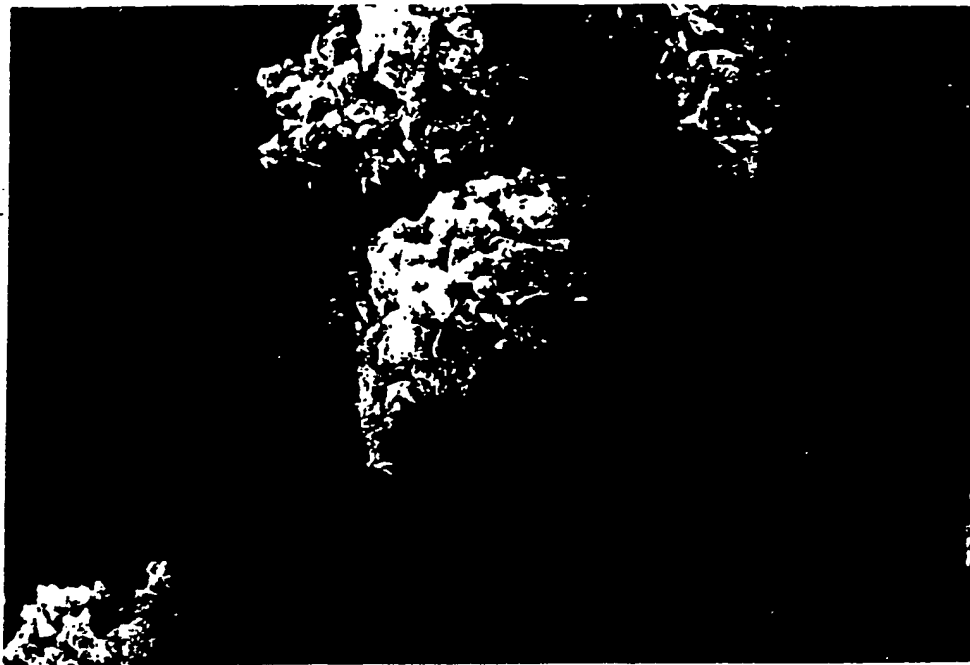


Fig. 2

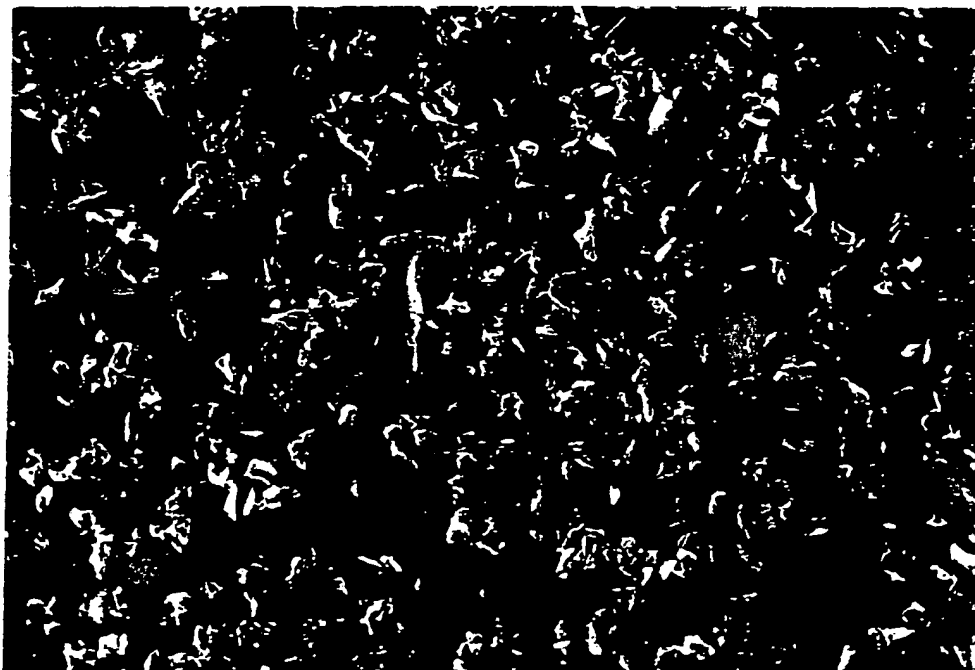


Fig. 1

2 / 5



Fig. 4



Fig. 3

SUBSTITUTE SHEET

3 / 5



Fig. 6



Fig. 5

SUBSTITUTE SHEET

4 / 5



Fig. 8



Fig. 7

SUBSTITUTE SHEET

5 / 5



Fig. 10



Fig. 9

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US90/00413

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5): C08F 265/02; C08K 7/02
 U.S. CL.: 525/243; 524/832

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷	
Classification System	Classification Symbols
U.S.	523/335; 524/813, 831, 832, 789, 792, 793; 525/243, 244, 254; 526/306, 317.1, 323.2
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸	

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A, 4,191,672 (SALOME ET AL.) 4 MARCH 1980, See the entire document.	12-13
A	US,A, 4,446,261 (YAMASAKI ET AL.) 1 MAY 1984, See the entire document.	12-13
Y	US,A, 4,647,617 (SAOTOME) 3 MARCH 1987, See column 1, lines 21 to 25, column 3, lines 30 to 57.	14-16
X Y	US,A, 4,708,997 (STANLEY, JR. ET AL.) 24 NOVEMBER 1987, see column 2, lines 24 to 68, column 3, line 28 to column 4, line 58, column 6, line 33 to column 7, line 8, column 8, lines 30 to 68.	<u>12-13</u>
A	US,A, 4,735,987 (MORITA ET AL.) 5 APRIL 1988 See the entire document.	12-13

^{*} Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

01 MARCH 1990

International Searching Authority

ISA/US

Date of Mailing of this International Search Report

11 APR 1990

Signature of Authorized Officer

R.H. DELMENDO